CHEMICAL AND PYROLYTIC THERMOGRAVIMETRIC CHARACTERIZATION OF NIGERIAN BITUMINOUS COALS

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Abstract

The discovery of new coal deposits in Nigeria presents solutions for nation's energy crises and prospects for socioeconomic growth and sustainable development. Furthermore, the quest for sustainable energy to limit global warming, climate change, and environmental degradation has necessitated the exploration of alternatives using cleaner technologies such as coal pyrolysis. However, a lack of comprehensive data on physico-chemical and thermal properties of Nigerian coals has greatly limited their utilization. Therefore, the physico-chemical properties, rank (classification), and thermal decomposition profiles of two Nigerian bituminous coals – Afuze (AFZ) and Shankodi-Jangwa (SKJ) – were examined in this study. The results indicate that the coals contain high proportions of *C, H, N, S, O* and a sufficiently high heating value (HHV) for energy conversion. The coal classification revealed that the Afuze (AFZ) coal possesses a higher rank, maturity, and coal properties compared to the Shankodi-Jangwa (SKJ) coal. A thermal analysis demonstrated that coal pyrolysis in both cases occurred in three stages; drying (30-200 °C), devolatilization (200-600 °C), and char decomposition (600-1000 °C). The results also indicated that pyrolysis at 1000 °C is not sufficient for complete pyrolysis. In general, the thermochemical and pyrolytic fuel properties indicate that the coal from both places can potentially be utilized for future clean energy applications.

Key words: Pyrolysis, Thermogravimetric, Bituminous, Coal, Nigeria.

1 INTRODUCTION

Nigeria is the Africa's largest economy, crude oil exporter, and the most populous nation. In addition, Nigeria also bears a distinct hallmark as the nation with the second largest coal deposits on the continent estimated at 4 billion tonnes [1]. Coal is therefore the most abundant fossil fuel in the country [2]. Furthermore, coal is the world's cheapest, most abundant, and widely distributed fossil fuel [3, 4]. It is estimated to account for 64 % of economically recoverable resources and is extensively utilized as fuel for electric power generation, cement production, and the manufacture of iron and steel worldwide [5].

With the discovery of large new coal deposits in nations like Nigeria, its importance as an industrial and commercial commodity will unquestionably increase in the future. However, the studies on the fuel properties and potential applications of the newly discovered coals in Nigeria are limited. Nonetheless, research on petrography, rheology, mineralogy, and geochemistry of Nigerian coal has been reported extensively [6-10]. The lack of data on the thermochemical fuel properties of the coals is an impediment to more accurate assessment of their technological applications and efficient industrial utilization [11-14]. With the demand for coal set to soar by 3% per annum, analysts predict that coal will account for 14.5 % of global energy mix in the next 20 years [15]. Yet, coal combustion emits significant proportions of CO_2 and greenhouse gases (GHGs) annually contributing to global warming, climate change, and environmental pollution.

With the ratification of the landmark Paris Agreement, the United Nations Framework Convention on Climate Change, the signatory countries have pledged to limit global warming to 1.5 °C by cutting greenhouse gas emissions (GHGs) from 46 billion to zero in 50 years [16]. Consequently, it is envisaged that GHGs can be reduced by concurrently investing in clean energy technologies and complete divestment from polluting technologies like conventional coal power generation. The proposed transition presents promising prospects for the development of sustainable conversion processes and clean coal technologies such as Integrated Gasification Combined Cycle (IGCC), Carbon Capture and Storage (CCS), Coal Pyrolysis and Gasification.

Pyrolysis is a potentially promising, sustainable conversion process for the valorization of carbonaceous fuels such as coal into clean fuels and power generation. Knowledge on the pyrolysis of the newly discovered coals is vital for the future implementation of clean coal technologies and applications. Despite all this, the thermochemical data on pyrolysis of the newly discovered Nigerian coal deposits and their properties is critically lacking in scientific literature.

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Therefore, the main objective of this paper is to characterize and examine the physico-chemical and thermal properties of the newly discovered Nigerian coals from Afuze (AFZ) and Shankodi-Jangwa (SKJ). The paper also presents novel data on the classification (rank), fuel properties, and pyrolytic decomposition profiles of coals as a fundamental requirement for assessing their future potential utilization. This is vital for the engineering design, modelling and optimization of thermochemical processes, conversion equipment, and environmental impact assessment of the newly discovered coals in Nigeria.

2 EXPERIMENTAL

The bituminous coal samples were obtained from the Afuze (AFZ) coal field, Edo State, Southern region and the Shankodi-Jangwa (SKJ) coal field, Nasarawa State, Middle Belt region of Nigeria. The samples were pulverised and sifted into 250 μm homogeneous sized particles. Subsequently, the coals were subjected to the ultimate analysis using the EL Vario MICRO Cube *Elementar* CNHS analyser to determine their elemental composition. The proximate analysis was examined based on the ASTM standard test techniques D3173, D3174, and D3175 for moisture, ash, and volatile matter, respectively. The oxygen and fixed carbon contents were determined by difference. The higher heating values (HHVs) of the coal samples were determined using a bomb calorimeter (Model: IKA C2000). All analyses were repeated at least three times to ensure reliability and reproducibility of the results. The classification of the coals according to the rank was examined using the ASTM D388-12 standard [5]. Next, the thermal analysis was carried out on the high precision Netzsch^{TM} TG 209 F3 thermogravimetric analyser using ultra-pure (99.99%) nitrogen as purge gas to ensure inert pyrolysis conditions. For each test, 9-12 mg of coal sample was weighed into an aluminium crucible and heated from 30-1000 °C at constant heating rate of 20 °C min^{-1}. The resulting .st6 data files from the thermal analyser were subsequently analysed using the Netzsch^{TM} proprietary software Proteus (v.6.1). The resulting data was plotted in MS Excel as weight loss (%) against temperature to examine the thermal decomposition behaviour of the coal samples under pyrolysis conditions. Lastly, the characteristic temperature profiles of the coals were deduced to determine the reactivity and potential application of the coals.

3 RESULTS AND DISCUSSION

3.1 Proximate and Ultimate Analysis

The ultimate and proximate analyses of the AFZ and SKJ coals are presented in Table 1 and compared with the values of other coals [18]. The results indicate that the coal samples comprise the appropriate elemental constituents typically observed in coal samples [17]. Furthermore, the coal samples contain significantly high proportions of *C, H, O* and lower amounts of *N* and *S*. However, the presence of *N* and *S,* albeit in minor proportions, may present operational challenges due to potential NO_x and SO_x emissions during the thermal conversion. Basically, the elemental contents of the coals were observed to be within the limits typically observed for coals in literature [18]. Furthermore, the higher values of *HHV, C, and* lower *H, M,* and *O* in the AFZ coal indicates a higher maturity and rank compared to the SKJ coal.

Tab. 1 Chemical Fuel Properties of Bituminous Nigerian Coals

Property (wt. %)	Symbol	AFZ (wt. %)	SKJ (wt. %)	Literature values [18]
Ultimate analysis				
Carbon	C	72.46	71.46	62.9 – 86.9
Hydrogen	H	6.07	6.40	3.5 – 6.3
Nitrogen	N	1.63	1.37	0.5 – 2.9
Sulphur	S	1.41	2.03	0.2 – 9.8
Oxygen	O	18.43	18.76	4.4 – 29.9
Proximate Analysis				
Moisture	M	1.97	5.14	0.4 – 20.2
Volatile Matter	VM	45.80	40.73	12.2 – 44.5
Ash	A	30.99	14.94	5.0 – 48.9
Fixed Carbon	FC	21.24	39.18	17.9 – 70.4
Heating value	HHV (MJ/kg)	30.52	27.34	16.0 – 34.0

Consequently, based on the fuel properties and HHV [5], the AFZ coal can be classified as High-Volatile B, Bituminous coal and the SKJ coal as High-Volatile C, Bituminous coal. Furthermore, the results indicate that the coals could be classified as High Rank Coals (HRC) with a potential for applications in power generation, the manufacture of cement, iron and steel.

3.2 Thermal Analysis

The thermal decomposition behaviour of the coals was investigated by a non-isothermal thermogravimetric analysis under pyrolysis conditions from room temperature to 1000 °C at heating rate of 20 °C min^{-1}. Figure 1 presents the downward sloping weight loss curves typically observed for thermally decomposing carbonaceous materials like coal and biomass under inert conditions [19-21].

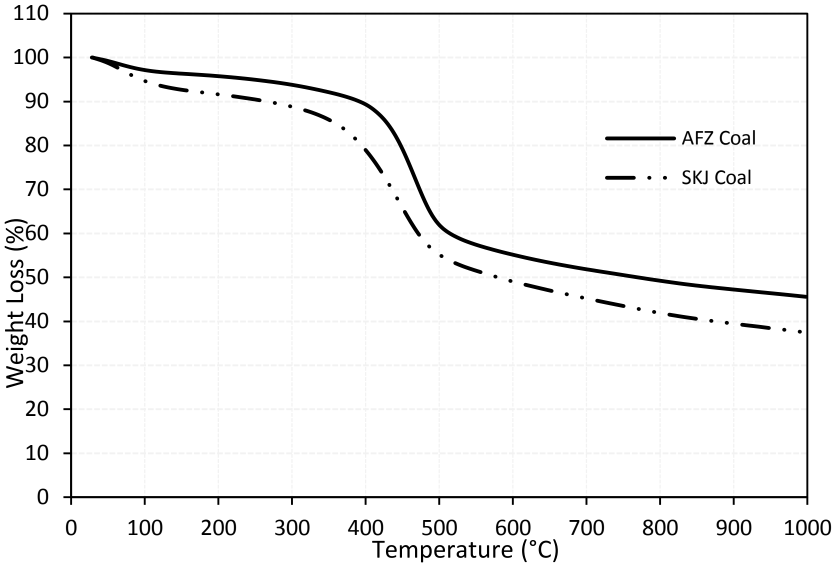

Fig. 1 TG Weight loss curves for AFZ and SKJ coals

Figure 1 revealed that heating the coal samples under the selected thermal reaction conditions resulted in incomplete pyrolysis. Consequently, 54.42 % of AFZ and 62.53 % of SKJ decomposed during the pyrolytic thermal analysis. Furthermore, the TG curves indicate that the SKJ coal sample is more reactive or less thermally stable than the AFZ coal, which is in good agreement with high reactivity typically observed for lower ranked coals (LRCs) [22]. This can be ascribed to the larger surface area, chemical composition, and presence of minerals in lower ranked coals that catalyse conversion reactions [23]. Furthermore, the LRCs possess a lower aromatic structure and smaller molecular nuclei which increases chemical reactivity during conversion [23, 24].

The reactivity of the coals can be further analysed by comparing the characteristic temperature profiles as presented in Table 2.

Tab. 2 Weight Loss Temperature profiles of AFZ and SKJ Coals

Coal Property	Onset (Ignition) Temperature T_{on} (°C)	End (Burnout) Temperature T_{end} (°C)	Total Coal Weight Loss T_d (%)
AFZ	416.90	505.30	54.42
SKJ	376.80	496.50	62.53

The results indicate that the ignition temperature of the SKJ coal at T_{on} = 376.80 °C is observably lower than that of AFZ at T_{on} = 416.90 °C. Similarly, the burnout temperature of the SKJ coal sample (T_{end} = 496.50 °C) is also lower than that of AFZ (T_{end} = 505.30 °C). The results further confirm that the AFZ coal is higher in rank and maturity than the more reactive SKJ coal. In comparison, the burnout temperatures for the AFZ and SKJ coals are considerably lower than 730–780 °C reported for other Nigerian coals [19]. The marked difference in T_{end} values may be due to variations in the rank, reactivity, and maturity of the coals.

3.3 Derivate Thermal Analysis

The DTG curves typically present the progressive decomposition of volatile organic matter and gaseous components evolved from the coal samples during the TGA [19]. Figure 2 presents the derivative weight loss (DTG) curves for the pyrolytic decomposition of the AFZ and SKJ coals.

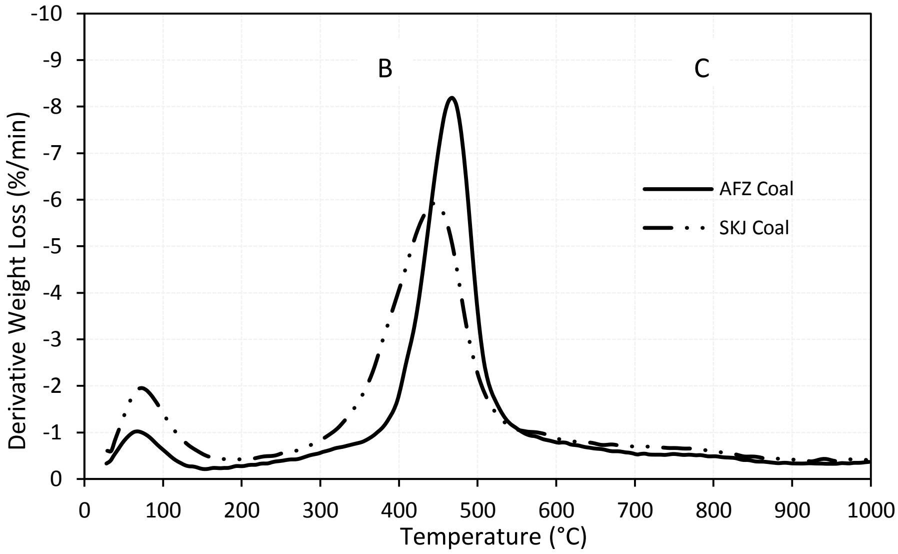

Fig. 1 Derivative Weight loss (DTG) curves for AFZ and SKJ coals

The decomposition of the coals displayed similar trends as indicated by the shape and orientation of the DTG peaks. Furthermore, the DTG curves each consist of two sets of endothermic peaks; the first between 30–200 °C, whereas the second was between 200–600 °C. Furthermore, the analysis of the peaks clearly specifies pyrolysis of the coals occurred in three stages; (A) 30–200 °C; (B) 200–600 °C; and (C) 600–1000 °C. Similar results have been observed for the pyrolysis of other coals [12, 19].

The first stage (A) corresponds to drying which denotes the loss of surface moisture, low volatile organic matter and mineral hydrates in the coals [12]. Comparatively, the SKJ coal moisture peak is evidently larger than that of the AFZ coal, which is due to its higher moisture content of 5.14 wt. % determined from the proximate analysis (Table 1). The second stage (B) (200–600 °C) can be attributed to the breakdown of the weak bonds of low volatile compounds due to the primary and secondary devolatization of the volatile matter. Consequently, the weight loss during devolatilization is significant, resulting in the evolution of CO, CO_2, CH_4, and other condensable gases [25]. The weight loss of the AFZ coal was 40.55 % with the maximum rate of decomposition T_{max} = 467.30 °C, whereas for the SKJ coal it was 42.55 %, at T_{max} = 445.70 °C. The results clearly show that the SKJ coal is of higher reactivity due to the higher weight loss observed during devolatization. Furthermore, the comparison of the weight loss during devolatization and the volatile matter content of the coals showed that the close correlation which confirms the stage B is due to the decomposition of volatile matter. Lastly, the final stage of devolatilization and weight loss was characterized by long tailing observed from 600 to 1000 °C and may be ascribed to the slow process of char degradation of the coals after devolatilization. The resulting mass of coal char for AFZ was 45.58 %, while that of SKJ was 37.47 %.

4 CONCLUSION

The proximate and ultimate analyses revealed that the Afuze (AFZ) coal possesses a high rank, maturity, and coal properties compared to the more reactive, lower ranked Shankodi-Jangwa (SKJ) coal. The thermal analysis demonstrated that pyrolysis of the coals occurred in three stages; drying (30-200°C), devolatilization (200-600°C), and char decomposition (600-1000°C). Furthermore, the results indicated that pyrolysis of the coals below 1000°C is inadequate for complete pyrolysis, hence higher temperatures are required. Lastly, the properties suggest the coals may have potential uses in power generation and the manufacture of cement, iron or steel.

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